

Alkali-Silica Reaction: Chemical Mechanisms, Thermodynamic Modeling, and the Effects of Lithium Ions

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ABSTRACT

The alkali-silica reaction (ASR) is one of the chemical distresses of concrete caused by reaction between reactive silica in aggregates and hydroxyl ions generated by alkalis present in the pore solutions. The product of the ASR (the alkali-silica gel) has the ability to imbibe water which, in turn, leads to its volume expansions. In many cases, this volume expansion is sufficient to cause cracking of the aggregates and the surrounding paste.

Despite over 70 years history of research in this area, the exact sequence of steps involved in ASR and the chemical nature of the gel are still not fully understood. Similarly, there is only limited information on the influence of the mineralogy of aggregates on the kinetics of the ASR process and the role of lithium ions in controlling the expansion.

To address some of these issues the present dissertation focused on four areas: a) chemical sequence and kinetics of the ASR processes, b) thermodynamic modeling of the chemical sequence of the ASR processes, c) the kinetics of alkali concentration in cementitious systems, and d) the exploration of the state of lithium ions in ASR systems.

The first part of this thesis describes results obtained from the study focused on the kinetics of physical and chemical changes in the reactive aggregate-simulated pore solution system undergoing ASR. Specifically, the study investigated the products formed by exposing reactive silica mineral (α -cristobalite) to the mixture of three alkali solutions and solid calcium hydroxide (Ca(OH)_2). The experimental results showed existence of a distinct chemical sequence (pattern) of the ASR processes: a) the formation of calcium silica hydrate, b) the formation of alkali binding polymerized calcium silica hydrate, c) the increase in concentration of silica ions in the solution, and d) the formation of ASR gels.

These experimental results were used to develop thermodynamic model for the chemical sequence and kinetics of the ASR processes, including the formulation of the kinetic rate law for silica

dissolution from the reactive silica minerals. This kinetic rate law accounts for such factors as pH, temperature, concentration of alkalis in solution, and type of the reactive silica mineral. Subsequently, the proposed kinetic rate law was used as an input to the commercial modeling software (Geochemist's Workbench[®]) to simulate the chemical sequence of the ASR processes. The model generated reasonably accurate predictions of the distribution of species in the reacting system and captured several distinct features of experimental data (i.e. depletion of $\text{Ca}(\text{OH})_2$, levels of alkali, silica concentrations, and pH levels).

In addition, the kinetics of concentration of alkali ions in real cementitious system (mortar) undergoing ASR was investigated. The results of these investigations not only confirmed that (as expected) the concentration of alkali ions in pore solution of the system undergoing ASR will decrease but, more importantly, it revealed that the rate of concentration change is linear with respect to the instantaneous (time dependent) concentration. This represents an important step in the development of the chemo-mechanical models as it experimentally confirms the validity of a commonly used assumption of the first order reaction as adequately representing the kinetics of the reaction process.

Finally, the thesis also presents the results of the study on the role of lithium ions in the ASR process. This study was performed using the following three experiments as follows: a) model reactor experiment (the reactive aggregate-simulated pore solution system undergoing ASR), b) the analysis of pore solution in mortars containing either reactive aggregate (Jobe sand) or non-reactive aggregate (Ottawa sand) with three different dosages of LiNO_3 (0, 0.26 and 0.74 of lithium to molar ratio), and c) the mortar bar expansion tests performed on specimens exposed to the same three different dosages of LiNO_3 as used in experiment b). The experimental results strongly support one of the previously proposed mechanisms for the role of Li^+ ions in controlling ASR. This mechanism involves the formation of the reaction products on the surface of the reactive aggregates, which prevents further hydroxyl ion attack of the particles. This part of study also revealed that the substantial loss of lithium ions from the pore solution during the hydration period is mainly the result of their incorporation in the newly developing hydration products. In addition, the results of this study were used to develop a model for prediction of the loss of lithium ions from the pore solution during the hydration period.

It is believed that the results of this research will provide useful components to the larger framework which will link the thermo-chemical model of the ASR processes with the mechanical degradation model.